MEASUREMENTS OF VAPOR PRESSURES OF HETEROATOM-CONTAINING PAH AND COAL-TAR MODEL MIXTURES

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INTRODUCTION

This paper presents the results of measurements of the vapor pressures of large polycyclic aromatic hydrocarbons (PAH), including those containing heteroatoms, and some mixtures of these compounds. The work was motivated by the lack of vapor pressure data on coal tars, which tend to have a highly aromatic nature and which also contain significant numbers of heteroatoms. Relatively few data are available on the vapor pressures of large polycyclics containing heteroatoms. Knowledge of coal tar vapor pressures is important in predicting the pyrolysis behavior of coals, since most advanced models of coal pyrolysis utilize an evaporation step to describe the loss of tar from the particles [1-8].

There have been some efforts made at characterizing vapor pressures of coal *liquids*, as opposed to coal tars [9]. For the most part, that work was concerned with relatively lighter compounds than are of interest in pyrolysis (typically, four fused aromatic rings or less, with molecular weights of about 300 or less). Primary coal tars exhibit molecular weights that are well over 1000 [1,6]. In addition, there is a tendency in liquefaction to reduce the heteroatom content of the coal liquids, so the important role of heteroatoms in determining properties of coal tars might not be well modeled by coal liquids. The predictive methods seen to work reasonably well with hydrocarbon model compounds for coal liquids were often noted to work more poorly in heteroatomic systems [9].

There is little hope of characterizing materials as complex as coal tars in very great detail. There is strong incentive to keep the amount of data needed for prediction of vapor pressures of such mixtures to an absolute minimum. This issue has historically been addressed by the use of correlations based upon molecular weight distributions alone [1-8,10,11], since molecular weight and temperature are the two most important variables in determining vapor pressures. These correlations have been of one particular form, obtained from the Clausius-Clapeyron equation, assuming that the heat of vaporization is a function of the molecular weight and not a function of temperature. The resulting form of correlation developed by Suuberg et al. [10] is :

$$P = \alpha \; \exp\!\left(-\beta \; \frac{M^\gamma}{T} \right)$$

This is the simplest expression which appears to be consistent with the known thermodynamics of the situation and is used because of the lack of detailed chemical structure and vapor pressure data on coal tar. It should also be noted, consistent with this approach, that it has been shown possible to correlate molecular weight of coal liquids using only boiling point information, at least up to about 400 molecular weight [9].

Several workers have employed such a correlation, and values of the constants they have obtained by fitting the data to literature data on aromatic hydrocarbons are shown below:

	α	β	γ
Suuberg et al.[10]	1.23×10^5	236	0.654
Suuberg et al.[11]	5765	255	0.586
Niksa [3]	70.1	1.6	1.0
Niksa and Kerstein [4]	3.0×10^5	200	0.6
Fletcher et al. [5]	87060	299	0.59
Oh et al. [8]	6.23×10^5	561	0.474

In this expression, P is in atmospheres, T is in K, and M is in daltons. Comparisons of the predictions of several of these models have been offered elsewhere [5]. Wide variations were noted in the predictions, and there is a concern about adequacy of predictions of the vapor pressures under pyrolysis conditions. Nevertheless, it is clear that there is a general convergence of most of the values of α, β, and γ in the literature. A comparison of the predictions of boiling point with molecular weight is shown in Figure 1, for various models. The results of Tsonopoulos et al. [9] and Fletcher et al. [5] are seen to be in good agreement, but this is not surprising, since they involved regression of many of the same data on coal liquids. For reference, the measured

properties of anthracene are indicated.

Most of the experimental data in the literature on what might be considered model compounds for coal tars have been measured in a pressure range from 10^{-4} to 10 torr. A problem arises in extrapolating existing experimental data out of the temperature range in which it was obtained. Measurements of vapor pressures of high molecular weight materials requires high temperatures to obtain conveniently measurable pressures, but high temperatures cannot be employed because of the concern about thermal decomposition during measurement. This, then, requires the use of moderate temperatures (<300°C) and sensitive, indirect vapor pressure measurement techniques. Yet it is the high temperature range (>300°C) that is of practical interest for coal tars, since these materials are formed at those high temperatures. Thus the extrapolation to high temperatures is of great importance. Significant concerns arise because many of the measurements must be performed with the compounds of interest in the solid phase, as opposed to the liquid phase in which they might exist at the high temperatures of practical interest. Thus the measurements are being conducted under *sublimation* conditions, whereas in practice, true evaporation will be occurring. This makes the prediction of changes in vapor pressure with temperature very difficult. Not only is a correction required to correct for sublimation as opposed to evaporation (involving an enthalpy of fusion), but the enthalpy of evaporation itself is a decreasing function of temperature.

In sublimation work, it is not uncommon to find that the Clausius-Clapeyron equation, with a constant $\Delta H_{sublimation}$, fits vapor pressure data reasonably well, i.e., $d [\ln P^{\circ}]/ d [1/T] = -\Delta H_{subl}/R$. The difficulty in developing reliable correlations of ΔH_{subl} with molecular weight is evident from the data of Figure 2, which shows data for high molecular weight aromatic hydrocarbons (a few containing heteroatoms). The poor correlation might be in part attributable to the difficulty of performing measurements by the indirect methods required. However, part of the difficulty might also be understood in terms of the enthalpy of sublimation consisting of contributions from the enthalpies of vaporization and fusion [12]. The enthalpies of vaporization of many compounds can be reasonably estimated by any number of means. The enthalpy of fusion, on the other hand, is very difficult to correlate with other properties [12]. For high molecular weight materials, the enthalpies of fusion can become comparable in magnitude to the enthalpies of vaporization. In this work, we are addressing this issue specifically, and will report on it separately.

EXPERIMENTAL

The vapor pressures of actual coal tars and model "tars", consisting of mixtures of PAH, are measured, using a molecular effusion/TGA technique. The various so-called "effusion" methods are based on the molecular effusion of a vapor from a surface, or through an orifice [13]. Of these methods, that which has been selected for use here is the Knudsen method [14,15], in which a substance of interest effuses through a small pinhole, of known area, in an otherwise sealed container or cell. The Knudsen method is used for the measurement of low vapor pressures in the range from 1 to 10^{-6} torr, under molecular flow conditions. This ideally requires that pressures inside and outside the sample cell are low enough that the frequency of collisions of vapor molecules with gas phase species are low in comparison with the frequency of collisions with the cell. The measurement of vapor pressure involves determining the rate of loss of molecules of the evaporating substance from the effusion cell under these conditions. Measurements are made under isothermal conditions, with weight loss from the cell being recorded as a function of time, generally in a TGA-type apparatus.

The basic theory of the effusion method has been often reviewed in the literature [14-16]. The theory of method is actually based upon the basic kinetic theory of gases. From these classical results, Knudsen derived an expression for the slow isothermal flow out of a cell with a small hole in it. The vapor pressure of a material in the cell can be calculated from Knudsen's original effusion rate result :

$$P_1 - P_2 = \frac{G}{t} \frac{w_1 + w_2}{\sqrt{\rho}}$$

where P_1 is the pressure of saturated vapor inside the cell, P_2 is the pressure outside of the effusion cell, w_1 is the resistance of hole in the cell, w_2 is the resistance of cell containing the sample, G is the mass lost by effusion, t is the effusion time, ρ is the density of the vapor at the temperature of experiment. The relation simplifies upon applying several simplifying assumptions, including the ideal gas law, that the pinhole leak is the main flow resistance, and assuming $P_1 \gg P_2$, yielding:

$$P = \frac{m}{t A_0} \left(\frac{2 \pi R T}{M} \right)^{1/2}$$

The above result is called the ideal Knudsen equation, in which P is the desired vapor pressure, m the mass loss during the effusion time interval , A_0 is orifice area, M the substance molecular weight , t the effusion time, and T the absolute temperature of the experiment. It is further assumed when applying this equation to the effusion process that the equilibrium vapor pressure of the effusing species obtains within the cell, that the orifice walls do not intercept and return into the cell an appreciable fraction of molecular current entering the hole, that there is no back flux into the orifice exit and the number of intermolecular collisions in the vapor phase occurring within the orifice is negligible.

In our implementation, the mass loss rate was continuously recorded, using a Cahn 2000 recording electrobalance. The cell containing the pinhole leak was suspended on one arm of the balance, which has nominal sensitivity in the μg level. The backpressure in the TGA system was maintained at 10^{-7} torr, which has been noted to be sufficient so as to provide accuracy in the 10^{-6} torr range of vapor pressures. The cell itself was maintained inside of a black capsule within the TGA, and was in close proximity to a thermocouple within the capsule. This was necessary in order to achieve the $0.1°K$ accuracy in temperature measurement required in vapor pressure work at low temperatures.

RESULTS AND DISCUSSION

Variation of Vapor Pressure with Temperature
Typical results are shown in Figure 3, for anthracene between 47 and 75 °C. The anthracene was of 99+% purity, purchased from Sigma Chemical Company, and used without further purification. Comparison is shown with other sources of data on this compound [17-21]. Again, the spread of the data is indicative of the difficulty in performing such measurements, on even relatively "easy" low molecular weight aromatics. The other feature which is clear from Fig. 3 is that the assumption that the enthalpy of sublimation is reasonable. Our results provide an enthalpy of sublimation of 101.6 kJ/mol. By way of comparison, the enthalpy of vaporization of anthracene, at its normal boiling point of 340 °C, is 56.5 kJ/mol [12]. The melting point of anthracene is 216°C, so our experiments were performed much below the melting point. This is, again, very clear indication of the danger in blindly extrapolating vapor pressure data over a wide range of temperatures. The actual extrapolation is shown in Figure 4. It is seen that the extrapolation leads to a reasonable prediction of the first reported point in the liquid region, since this was very close to the melting point of the anthracene. As one extrapolates into the liquid region, the comparison becomes progressively poorer, because $\Delta H_{subl} \neq \Delta H_{vap}$. If one considers the earlier suggested correction of the enthalpy of sublimation to the enthalpy of vaporization, the enthalpy of fusion would be around 45 kJ/mol. The ratio of the enthalpy of fusion to the enthalpy of vaporization is roughly 0.8, which is quite close to the the same ratio for n-dodecane (0.84 [12]), the normal alkane with a molecular weight closest to that of anthracene.

Mixture Models
It is unclear what mixture models can be used to describe vapor-liquid equilibrium for tars, which are obviously multicomponent mixtures. Typically, the most common assumption is Raoult's Law, in which the tar mixture is assumed ideal. There have been no attempts to establish how reasonable this assumption might be. Nearly ideal mixing behavior was seen for aromatic hydrocarbon mixtures (e.g. anthracene and perylene). An example of how a simple mixture model might badly fail is provided in Figure 5, for a mixture of phenanthridine and 1-hydroxypyrene. Aromatics containing such functional groups would be expected in coal tars. It would be anticipated that there would be strong acid-base interaction in this case, and this is clearly shown by the fact that the vapor pressure is far lower than predicted by Raoult's Law. Clearly more work is needed to establish how closely Raoult's Law might be followed in real tars.

ACKNOWLEDGMENT

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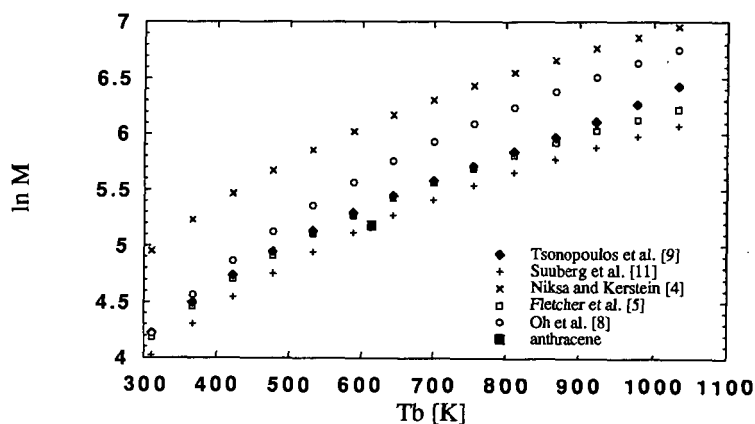21. Sonnefeld,W.J., *Anal. Chem., 55*, 275 (1983).

Figure 1. Predicted variation of boiling point with molecular weight, for low molecular weight aromatics.
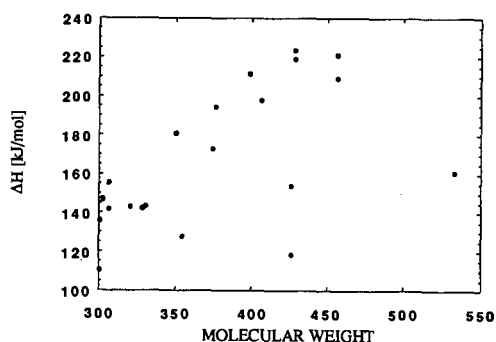

Figure 2. Variation of enthalpies of sublimation with molecular weight of aromatics. Data from *Handbook of the Thermodynamics of Organic Compounds*, by R.M. Stephenson and S. Malanowski, Elsevier, 1987.
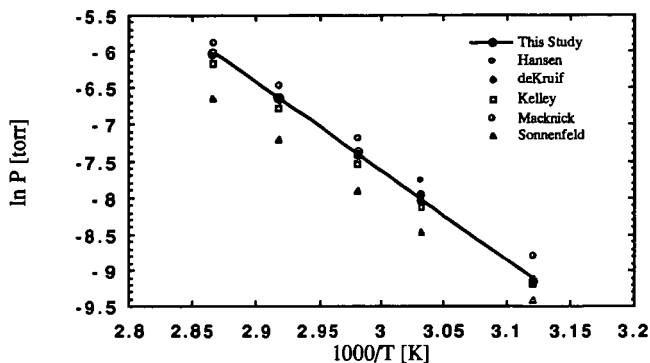
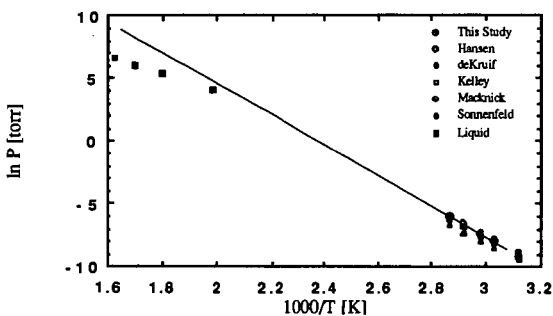Figure 3. Vapor pressures of solid anthracene, from this study and the literature.

Figure 4. Vapor pressures of solid and liquid anthracene. Liquid data from Stephenson and Malanowski.
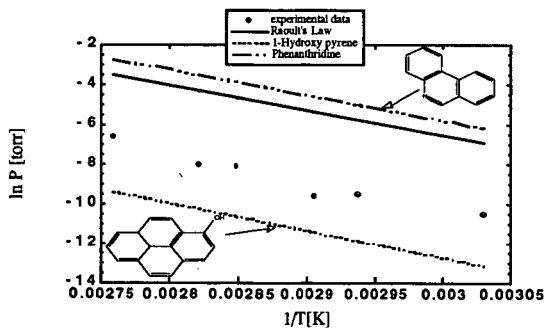

Figure 5. Vapor pressures of 1-hydroxypyrene, phenanthridine, and a mixture of 54 mol% 1-hydroxypyrene, 46% phenanthridine. The Raoult's Law prediction for the mixture is also shown.